ORGANOMETALLICS

Article

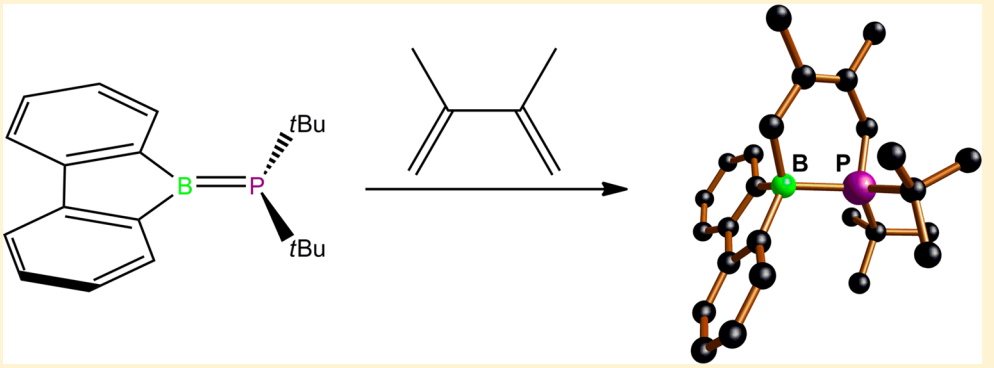
pubs.acs.org/Organometallics

Reactivity of Phosphaboradibenzofulvene toward Hydrogen, Acetonitrile, Benzophenone, and 2,3-Dimethylbutadiene

Jens Michael Breunig, Alexander Hübner, Michael Bolte, Matthias Wagner, and Hans-Wolfram Lerner*

Institut für Anorganische Chemie, Goethe-Universität Frankfurt am Main, Max-von-Laue-Straße 7, 60438 Frankfurt am Main, Germany

Supporting Information



ABSTRACT: The reaction of 9-bromo-9-borafluorene (**1**) with Li[P*t*Bu$_2$] in toluene gave quantitatively the corresponding di-*tert*-butyl-phosphaboradibenzofulvene (9-di-*tert*-butylphosphanyl-9-borafluorene, **2**). Degradation of thf occurred by treatment of **2** with thf in toluene at room temperature. In this paper the reaction of **2** with gaseous H_2 in toluene solution at room temperature is described, by which the corresponding H_2 addition product **4** was formed. The hydrogen addition product **4** crystallizes from benzene in the monoclinic space group $P2_1/n$. Addition reactions of **2** with acetonitrile, benzophenone, and 2,3-dimethylbutadiene were also investigated. Treatment of **2** with a 20-fold excess of acetonitrile afforded the corresponding adduct, which itself dimerized to a mixture of *cis* and *trans* isomers of the corresponding cycloiminoborane **6**. Cocrystals of *cis*-**6** and *trans*-**6** (ratio 2:1) were obtained from toluene in the presence of 20 equiv of acetonitrile at 6 °C (monoclinic space group $P2_1/c$). The isolation of the pure *trans*-**6** was achieved from toluene in the presence of 2 equiv of acetonitrile at −30 °C (triclinic space group $P\bar{1}$). Benzophenone reacted with the phosphaboradibenzofulvene **2**, forming the corresponding addition product **7** (orthorhombic space group *Pbca*). The reaction of **2** with a 6-fold excess of 2,3-dimethylbutadiene gave the related Diels−Alder adduct **8** (monoclinic space group $P2_1/c$).

INTRODUCTION

Unsaturated BP compounds with two and four substituents are rare, and only a few of these compounds were characterized by X-ray crystallography.[1−11] In most cases sterically bulky substituents are necessary to suppress cyclization or oligomerization. In spite of the use of very bulky substituents, the preparation of boranylidene phosphanes has still not yet been possible. Nöth and co-workers, however, could isolate the boranylidene phosphane complex (TMP)B═P(CEt$_3$)(Cr(CO)$_5$) (TMP = 2,2,6,6-tetramethylpiperidino), by which the Lewis-basic P center coordinates to the electrophilic Cr(CO)$_5$ fragment.[6] As a consequence, this complexed boranylidene phosphane displays an allene structure in the solid state.[6] Recently Power et al. have reported that the DMAP-supported boranylidene phosphane (DMAP)(TMP)B═PAr (Ar = 2,6-(2,4,6-*i*Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$; DMAP = 4-dimethylaminopyridine) can be synthesized by the reaction of ArPH-BBr(TMP) with 2 equiv of DMAP.[7] In this compound the Lewis-acidic B center is additionally coordinated by one DMAP molecule.[7] Generally, phosphinoboranes possess three-coordinate B and P centers. This structural feature was also realized in the solid-state structures of several triphosphatriborinane ring dervatives, BP cumulenes with allene or butadiene structures, and borylated lithium phosphides.[3,5]

A characteristic feature of boranylidene phosphanes as well as of phosphinoboranes is that they have a strong tendency to associate, in a head-to-tail manner, to give rings or oligomers (BX$_2$PR$_2$)$_n$, which have BP frameworks consisting of four-coordinate B and P centers. The ring size of cyclophosphinoboranes (BX$_2$PR$_2$)$_n$ depends on the method of preparation and on the nature of the substituents R and X.[12]

Generally, phosphinoboranes exhibit spectroscopic and structural evidence of significant BP π-bonding. It was reported

Special Issue: Applications of Electrophilic Main Group Organometallic Molecules

Received: June 14, 2013

   dx.doi.org/10.1021/om400553j | *Organometallics* XXXX, XXX, XXX−XXX

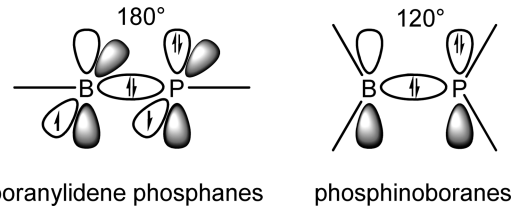


Figure 1. BP compounds with two and four substituents.

that the BP bond lengths in phosphinoboranes, e.g., $(C_6F_5)_2B{=}PtBu_2$,[11] with electron-withdrawing ligands are much shorter than those observed for the analogous compounds $(Mes)_2B{=}PR_2$[2] (R = *t*Bu, Ph, Mes), in which the B atom is coordinated by electron-rich mesityl groups. Calculations reveal that the π-bonding HOMOs in the phosphinoboranes were highly polarized (e.g., $(C_6F_5)_2B{=}PtBu_2$: 74% of the HOMO derived from the P atom but only 26% from the B atom).[11] Additionally, Stephan et al. have reported that the phosphinoboranes with pentafluorophenyl substituents $(C_6F_5)_2B{=}PR_2$ (R = *t*Bu, Cy, Mes; Cy = cyclohexyl) activate hydrogen due to the ambiphilic character of their BP units.[10,11]

It is remarkable that the structural analogy of phosphinoboranes and silenes (1.786−1.859 Å for B=P[2,11] and 1.702−1.764 Å for Si=C[13−15]) implies that the π-bonds in phosphinoboranes are similar to those in silenes. Therefore the isoelectronic phosphinoborane $(C_6F_5)_2B{=}PtBu_2$ is thus, in a sense, a mirror of Wiberg's silene.

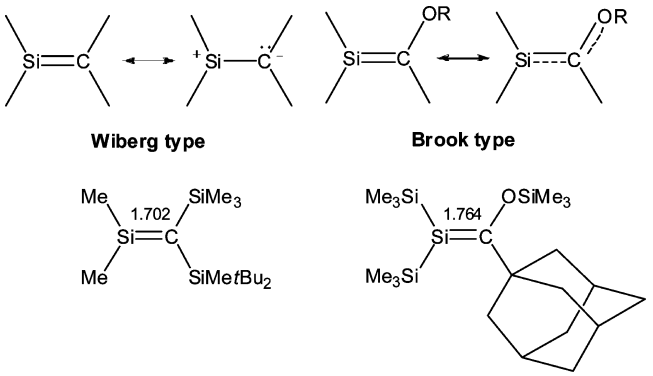


Figure 2. Comparison Wiberg-type and Brook-type silenes.

In this context it should be noted that silenes of the Wiberg type possess a more polar and shorter double bond than silenes of the Brook type.[15] Moreover it was reported that silenes of the Wiberg type are more reactive than Brook-type silenes.[15] In contrast to the well-known reactivity of silenes toward enes and dienes,[16] electrocyclic reactions of phosphinoboranes have rarely been studied up to now.

In the course of our investigations of unsaturated boron compounds and boraaromatics we could demonstrate the antiaromatic nature of borafluorene.[17,18] This predicts very Lewis-acidic B centers for this class of compounds. Therefore we decided to synthesize phosphinoboranes with borafluorene moieties (phosphaboradibenzofulvene) and to investigate their reactivity.

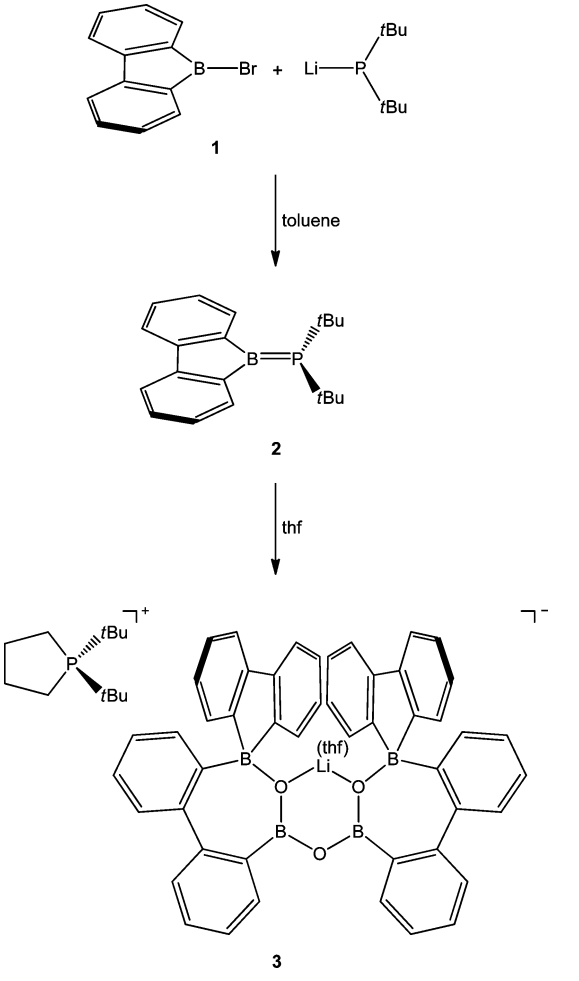
Concretely we present the synthesis of the phosphaboradibenzofulvene **2** in this paper. Further, a comparison of the hydrogenation of the BP bond of phosphaboradibenzofulvene **2** to that of Stephan's phosphinoboranes $(C_6F_5)_2B{=}PR_2$ (R = *t*Bu, Cy, Mes) was made. Finally we report on addition reactions of the phosphaboradibenzofulvene **2** with acetonitrile, benzophenone, and 2,3-dimethylbutadiene (DMB), by which the related trapping products could be isolated.

RESULTS AND DISCUSSION

When 9-bromo-9-borafluorene (**1**)[19] in toluene was treated with one molar equiv of $Li[PtBu_2]$,[20] the reaction mixture underwent a color change to red, while the NMR spectra of the solution revealed new signals. These signals could be assigned to phosphaboradibenzofulvene **2**. After filtering and removing the solvent, **2** was obtained as a red oil. In this context it should be noted that the physical properties of the phosphaboradibenzofulvene **2** are comparable with those of the carbon analogues.[21] The phosphinoboranes $(C_6F_5)_2B{=}PR_2$ (R = *t*Bu, Cy, Mes) are yellow compounds, whereas the phosphaboradibenzofulvene **2** has an impressive red color. The UV−vis spectrum of **2** is characterized by a broad absorption band at λ_{max} = 478 nm (Figure 5S in the Supporting Information).

In addition we decided to prepare the thf-supported phosphaboradibenzofulvene from **2** and thf; however, this approach failed. Instead of thf-complexed **2** we isolated the phosphonium salt **3** by this reaction, as shown in Scheme 1. Apparently, the phosphaboradibenzofulvene **2** is able to initiate

Scheme 1. Reactions of the Bromoborafluorene 1 with $Li[PtBu_2]$: Synthesis of Phosphaboradibenzofulvene 2 and the Formation of the Phosphonium Salt 3

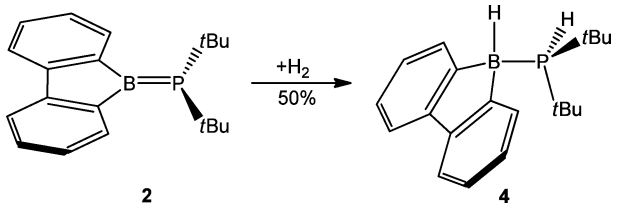


dx.doi.org/10.1021/om400553j | *Organometallics* XXXX, XXX, XXX−XXX

degradation of thf by which the O atom (formal as O^{2-}) of the thf molecule is transferred to the B center and the butylene unit (formal as $C_4H_8^{2+}$) of thf to the phosphanyl group of the phosphaboradibenzofulvene.

The phosphaboradibenzofulvene **2** is a highly reactive compound, and we considered that it has the potential for hydrogenation of the BP bond. When a solution of **2** in toluene was stirred at room temperature in an atmosphere of H_2 (1 atm), the red color of **2** disappeared after two hours. We therefore concluded that H_2 addition took place. In addition the signals of **2** were no longer recognizable in the NMR spectra of the reaction solution. Instead, resonances in the ^{11}B and ^{31}P NMR spectra, showing ^1J couplings to H atoms, were attributable to the H_2 addition product **4**. Unfortunately we could not isolate **4** by this approach. However, identification of **4** was confirmed by an independent synthesis, as treatment of 9*H*-9-borafluorene with HP*t*Bu$_2$ yielded quantitatively the adduct **4**. Interestingly, the phosphaboradibenzofulvene **2** apparently reacts faster with H_2 than the related phosphinoborane $(C_6F_5)_2B{=}PtBu_2$[10] does (reaction time: 1 d vs 4 weeks at room temperature). From this we can conclude that the polarity of the BP bond of **2** and therefore the Lewis acidity caused by the B center of the borafluorene moiety are higher than those of the $(C_6F_5)_2B$ group in $(C_6F_5)_2B{=}PtBu_2$.

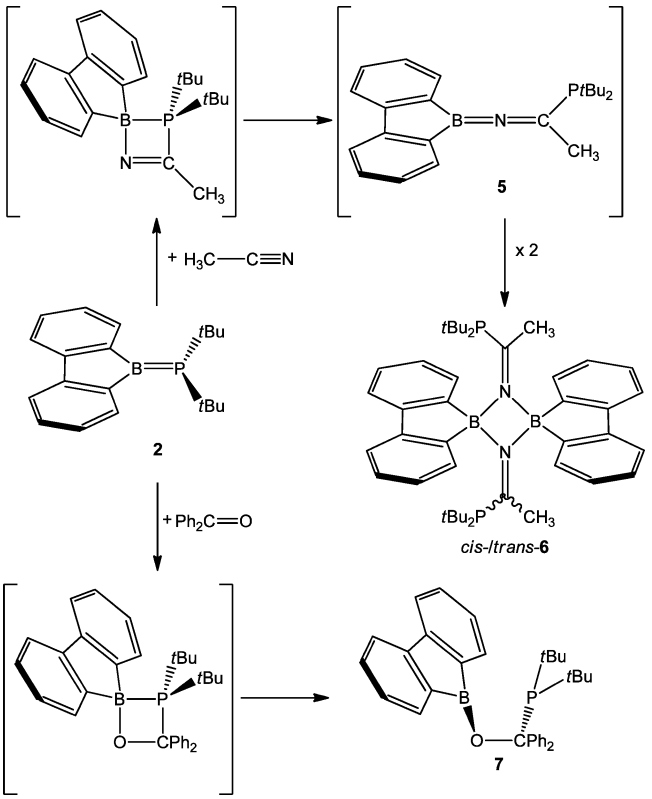
Scheme 2. Reaction of Phosphaboradibenzofulvene 2 with H_2



If indeed the BP bond in **2** possesses π-character, it should be possible to trap phosphaboradibenzofulvene **2** by addition of enes or dienes. This was attempted with acetonitrile, benzophenone, and DMB. These compounds have long been known to be excellent trapping agents for the silicon−carbon double bond.[16] Treatment of **2** with a 20-fold excess of acetonitrile at ambient temperature afforded the related trapping product **6** (Scheme 3). The formation of **6** suggested to us the mechanism, as shown in Scheme 3: (i) The [2+2] cycloadduct is formed. (ii) Then, the transient [2+2] cycloadduct undergoes ring-opening to give the azaboraallene **5**, which (iii) itself dimerizes to **6**. The cyclodiboradiazane **6**, which results from a [2+2] cycloaddition of azaboraallene **5**, was identified from its NMR spectroscopic characteristics; specifically the shift in the ^{11}B NMR (δ = 7.4) spectrum is in the range of already known four-membered B_2N_2 rings.[26] The most striking observation on the reaction of **2** with acetonitrile is that *cis* and *trans* isomers of **6** are formed. Cocrystals of *cis*-**6** and *trans*-**6** in the ratio 2:1 were obtained from toluene in the presence of 20 equiv of acetonitrile at 6 °C (monoclinic space group $P2_1/c$). Pure *trans*-**6** was isolated from toluene in the presence of 2 equiv of acetonitrile at −30 °C.

The phosphaboradibenzofulvene **2** reacted rapidly with benzophenone, forming the corresponding trapping product **7**, which could be isolated from the reaction solution. The ^{13}C NMR spectrum of **7** reveals a characteristic resonance of 94.6

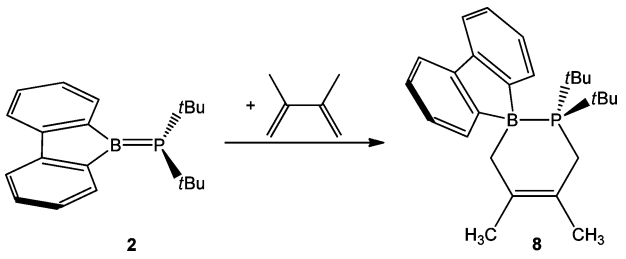
Scheme 3. Reaction of the Phosphaboradibenzofulvene 2 with Acetonitrile and Benzophenone



ppm for a C-OB nucleus. Furthermore, the ^{11}B shift (46.9 ppm) of **7** is in the range that was found for borinic esters.

By the reaction of **2** with a 6-fold excess of DMB the [4+2] cycloadduct **8** was formed (Scheme 4). The Diels−Alder

Scheme 4. Reaction of the Phosphaboradibenzofulvene 2 with 2,3-Dimethylbutadiene



adduct **8** was identified from its NMR spectra. The ^{13}C NMR spectrum of Diels−Alder adduct **8** displays resonances at 117.6 and 136.7 ppm, which could be assigned unambiguously to a C=C double bond. Additionally the structure of **8** was confirmed by X-ray structure analysis. In 2007 Gilbert and Bacharach have calculated that the phosphinoborane $(F_3C)_2B{=}PtBu_2$ undergoes facile [2+2] cycloadditions with acetylene and ethene as well as [4+2] cycloadditions with butadiene derivatives.[22,23] Indeed, we were successful in preparing and isolating the trapping products of **2** with $CH_3C{\equiv}N$ and $Ph_2C{=}O$ as well as the [4+2] cycloaddition product of **2** with 2,3-dimethylbutadiene.

The connectivity of the thf degradation product **3** (Scheme 1) is supported by an X-ray diffraction study, the quality of

dx.doi.org/10.1021/om400553j | *Organometallics* XXXX, XXX, XXX−XXX

which prevents its publication. A ball-and-stick presentation (Figure 3S) can be found in the Supporting Information.

The hydrogen addition product **4** shown in Figure 3 crystallizes in the monoclinic space group $P2_1/n$ (for selected bond lengths and angles, see in the figure caption). As anticipated, the structure of **4** has pseudotetrahedral P and B centers. The B−P bond length of 1.9733(16) Å in **4** is comparable with that found in $(C_6F_5)_2$BH-PH*t*Bu$_2$ (1.966(9) Å). It is interesting that the B−P bond lengths of **4** as well as those of Stephan's hydrogen addition products $(C_6F_5)_2$BH-PHR$_2$ (R = Et, *t*Bu, Cy, Ph, Mes) are significantly shorter (∼0.1 Å) than the B−P bonds of related dialkylphosphane borane adducts.[24] The molecular structures of $(C_6F_5)_2$BH-PHR$_2$ (R = Et, *t*Bu, Cy, Ph, Mes)[11] reveal a *trans* orientation of the B−H and P−H hydrogen atoms, whereas the solid-state structure of **4** exhibits a typically staggered conformation with *syn* arrangement of the hydrogen atoms and a H−B−P−H torsion angle of −81(1)°.

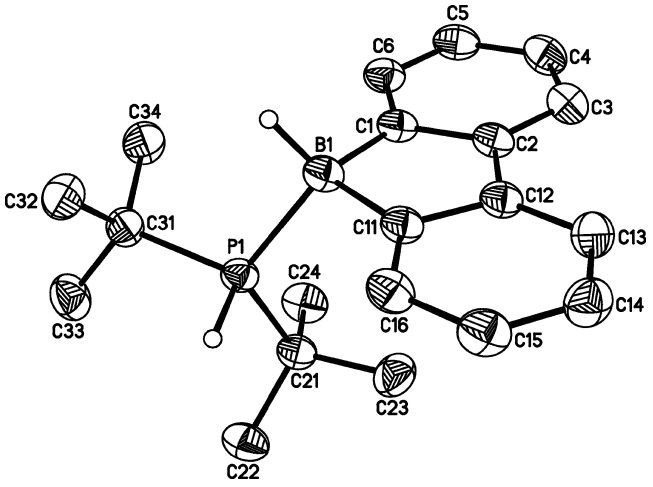


Figure 3. Solid-state structure of the H_2 addition product **4** (monoclinic, $P2_1/n$). Displacement ellipsoids are drawn at the 50% probability level. H atoms, except for the two freely refined H atoms on B1 and P1, are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): B(1)−C(1) = 1.617(2), B(1)−C(11) = 1.615(2), B(1)−P(1) = 1.9733(16), P(1)−C(21) = 1.8593(14), P(1)−C(31) = 1.8624(14); C(1)−B(1)−C(11) = 100.35(11), C(1)−B(1)−P(1) = 117.36(10), C(11)−B(1)−P(1) = 108.36(9), C(21)−P(1)−C(31) = 115.15(7), C(21)−P(1)−B(1) = 116.25(6), C(31)−P(1)−B(1) = 112.11(7).

Cocrystals of *cis*-**6** and *trans*-**6** in the ratio 2:1 were obtained from toluene in the presence of 20 equiv of acetonitrile at 6 °C (monoclinic space group $P2_1/c$). The crystal structure of *cis*-**6** is shown in Figure 4 and that of *trans*-**6** in Figure 6; selected bond lengths and angles can be found in the corresponding captions (crystal packing of cocrystallized *cis*-**6** and *trans*-**6** is shown in Figure 5). Crystallization of pure *trans*-**6** was achieved from toluene in the presence of 2 equiv of acetonitrile at −30 °C (triclinic space group $P\bar{1}$, Figure 6 and Figure 1S in the Supporting Information). The central core of both isomers of **6** is formed by a four-membered B_2N_2 ring (ring angles of *cis*-**6**: B−N−B = 93.3(3)° and N−B−N = 86.2(3)°; ring angles of *trans*-**6**: B−N−B = 93.5(3)° and N−B−N = 86.5(3)°). The N atoms are thereby part of an imino group. The C═N bond lengths of the imino units of *cis*-**6** as well as of *trans*-**6** are consistent with a full C═N double bond.[24] As expected, the atoms directly linked to each C═N unit are coplanar. It is

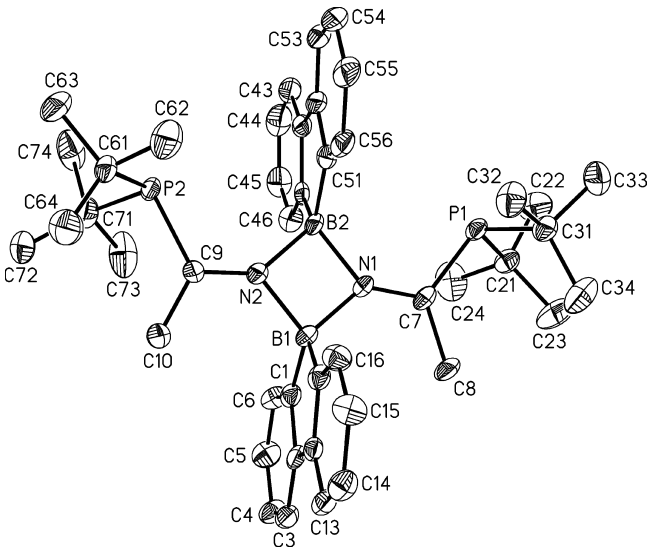


Figure 4. Solid-state structure of *cis*-**6**, which was obtained from the reaction of **2** with acetonitrile (monoclinic, $P2_1/c$). Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg): B(1)−N(1) = 1.581(7), B(1)−N(2) = 1.591(6), B(2)−N(1) = 1.608(6), B(2)−N(2) = 1.596(6), N(1)−C(7) = 1.296(6), N(2)−C(9) = 1.287(6), P(1)−C(7) = 1.844(5), P(2)−C(9) = 1.872(5), C(7)−C(8) = 1.518(6), C(9)−C(10) = 1.482(7); N(1)−B(1)−N(2) = 87.2(3), N(1)−B(2)−N(2) = 86.2(3), B(1)−N(1)−B(2) = 93.3(3), B(1)−N(2)−B(2) = 93.3(3), B(2)−N(1)−C(7) = 137.4(4), B(1)−N(1)−C(7) = 129.3(4), N(1)−C(7)−P(1) = 118.4(3), N(1)−C(7)−C(8) = 116.6(5), N(2)−C(9)−P(2) = 117.2(4), N(2)−C(9)−C(10) = 117.8(4); B(1)−N(1)−C(7)−P(1) = −176.9(4), B(2)−N(1)−C(7)−P(1) = 4.6(9), B(1)−N(2)−C(9)−P(2) = −178.5(4), B(2)−N(2)−C(9)−P(2) = −0.2(9).

interesting to note that in contrast to the already structurally characterized cycloiminoboranes,[25,26] which feature a *trans* orientation of their substituents, for the first time a cycloiminoborane derivative had been structurally characterized that displays a *cis* arrangement of its imino residues.

The benzophenone trapping product **7** (shown in Figure 7; for selected bond lengths and angles, see the figure caption) crystallizes in the orthorhombic space group *Pbca*. The trapping product **7** consists of one borafluorene moiety and one *t*Bu$_2$P group, which are connected by a central benzophenone unit. As shown in Figure 7, the borinic acid ester **7** possesses a staggered configuration with *anti* arrangement of borafluorene and *t*Bu$_2$P substituents (B−O−C−P torsion angle of −171.6(3)°).

The [4+2] cycloadduct **8**, shown in Figure 8, crystallizes in the monoclinic $P2_1/c$ space group (selected bond lengths in the caption of Figure 8). Crystals of **8** were grown from a concentrated toluene/pentane (1:1) solution at −30 °C. The central structure motif of **8** is a heterocycle that is composed of one P and one B atom and a 2-butenyl unit. In this structure the BPC_4 ring possesses a twist conformation. The B−P bond length of 1.9882(17) Å in **8** varies only slightly from that found in **4** (1.9733(16) Å). All other structural parameters of **8** are in the expected range.[24]

CONCLUSION

In summary, the reaction of the bromoborafluorene **1** with Li[P*t*Bu$_2$] yielded quantitatively the phosphaboradibenzofulvene **2**. We found that degradation of thf occurred by treatment of **2** with thf in toluene at room temperature.

dx.doi.org/10.1021/om400553j | *Organometallics* XXXX, XXX, XXX−XXX

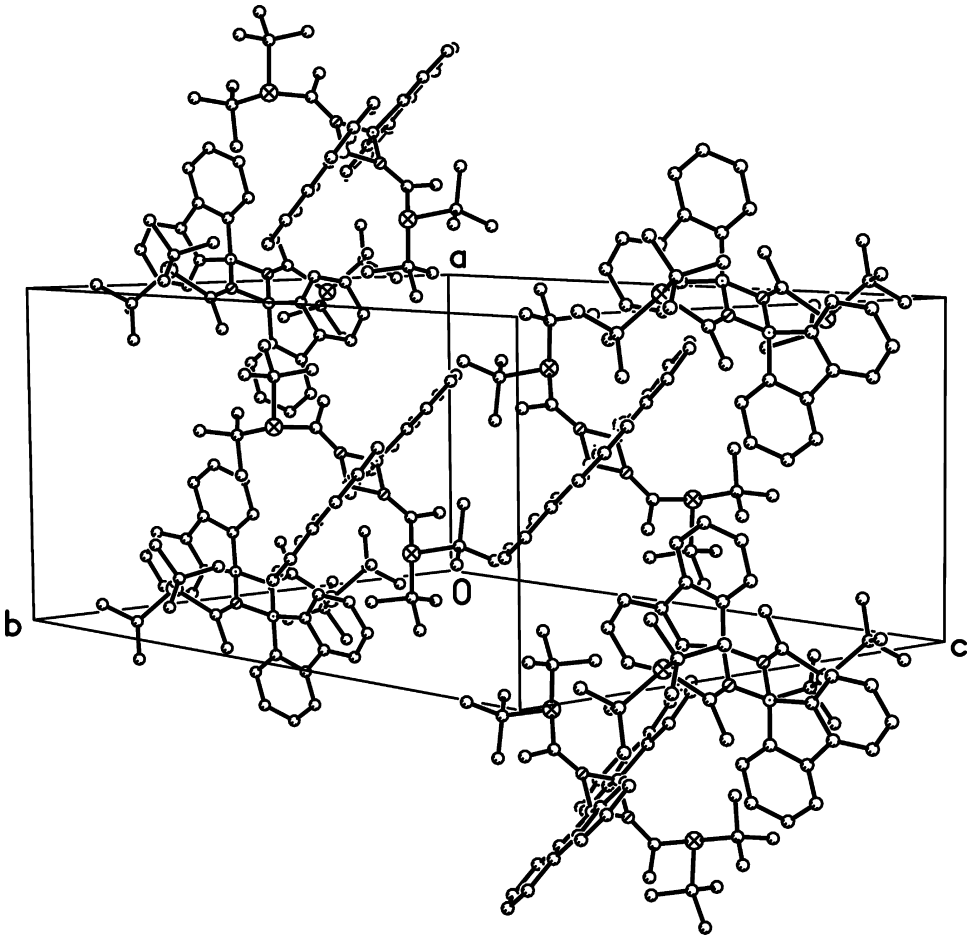


Figure 5. Crystal packing of cocrystallized *cis*-**6** and *trans*-**6** (ratio 2:1; monoclinic, $P2_1/c$).

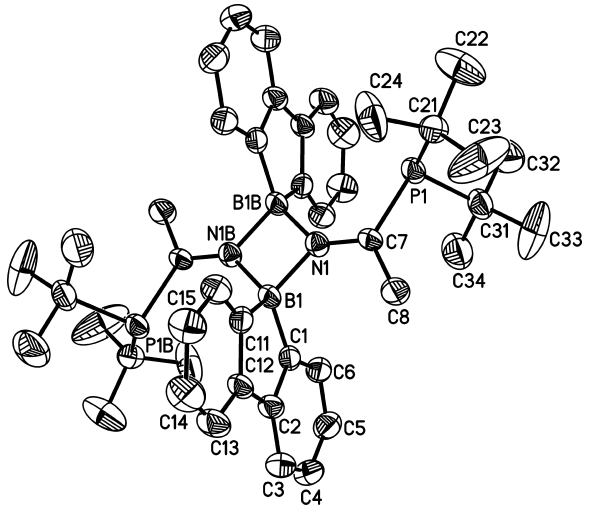


Figure 6. Solid-state structure of the cycloiminoborane *trans*-**6** (triclinic, $P\bar{1}$). Selected bond lengths (Å) and bond angles (deg): B(1)−N(1) = 1.577(6), N(1)−C(7) = 1.272(6), P(1)−C(7) = 1.866(5), C(7)−C(8) = 1.522(5); N(1)−B(1)−N(1B) = 86.5(3), B(1)−N(1)−B(1B) = 93.5(3), B(1)−N(1)−C(7) = 131.4(3), N(1)−C(7)−P(1) = 116.7(3), N(1)−C(7)−C(8) = 118.7(4); B(1)−N(1)−C(7)−C(8) = −4.2(7), B(1)−N(1)−C(7)−P(1) = 175.6(4). Symmetry transformation used to generate equivalent atoms: B $-x+1, -y+1, -z+1$.

Our investigation of the chemical behavior of the phosphaboradibenzofulvene **2** indeed confirms the ambiphilic character of its BP bond. This could be impressively demonstrated in the reaction of **2** with gaseous H_2 in toluene solution at room temperature, by which the H_2 addition product **4** was formed. Moreover we have shown addition reactions of the phosphaboradibenzofulvene **2** with acetonitrile, benzophenone, and 2,3-dimethylbutadiene. Therefore the chemical behavior of **2** is comparable to that of Wiberg-type silenes. Treatment of **2** with a 20-fold excess of acetonitrile afforded at first the azaboraallene **5**. However, this compound undergoes dimerization to give the corresponding cycloiminoborane **6** as a mixture of *cis* and *trans* isomers. Cocrystals of *cis*-**6** and *trans*-**6** in the ratio 2:1 were obtained from toluene in the presence of 20 equiv of acetonitrile at 6 °C, whereas pure *trans*-**6** could be isolated from toluene in the presence of 2 equiv of acetonitrile at −30 °C. Benzophenone reacted rapidly with the phosphaboradibenzofulvene **2**, forming the corresponding trapping product **7**. The reaction of **2** with a 6-fold excess of 2,3-dimethylbutadiene yielded the Diels−Alder adduct **8**. We reported in this paper the isolation and X-ray crystal structure of **8**, which to our knowledge is the first structurally characterized phosphinoborane Diels−Alder adduct.

EXPERIMENTAL SECTION

General Procedures. All reactions and manipulations were carried out under dry, oxygen-free nitrogen by using standard Schlenk

dx.doi.org/10.1021/om400553j | *Organometallics* XXXX, XXX, XXX−XXX

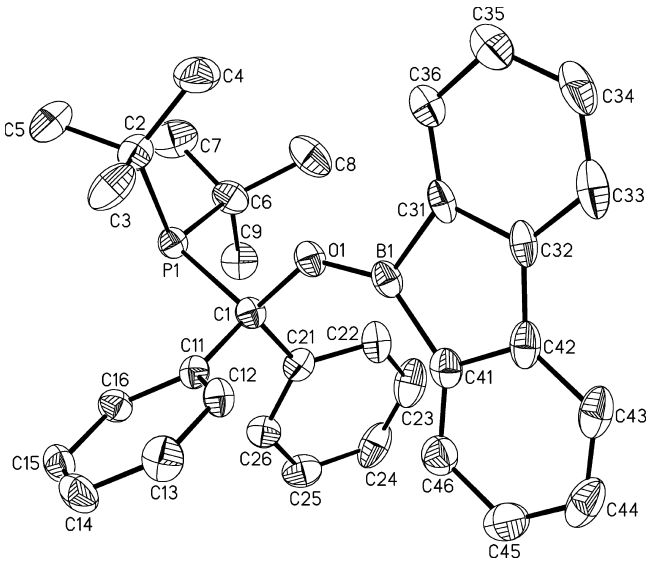


Figure 7. Solid-state structure of the trapping product **7**, which was obtained from the reaction of **2** with benzophenone (orthorhombic, *Pbca*). Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg): B(1)−O(1) = 1.357(5), B(1)−C(31) = 1.578(6), B(1)−C(41) = 1.580(6), O(1)−C(1) = 1.452(4), P(1)−C(1) = 1.944(4), C(1)−C(11) = 1.545(5), C(1)−C(21) = 1.532(5); C(31)−B(1)−C(41) = 104.7(3), O(1)−B(1)−C(31) = 119.8(4), O(1)−B(1)−C(41) = 135.5(3), B(1)−O(1)−C(1) = 131.2(3), P(1)−C(1)−O(1) = 109.9(2), C(11)−C(1)−C(21) = 111.2(3); B(1)−O(1)−C(1)−P(1) = −171.6(3).

techniques or in an argon-filled M. Braun glovebox. The solvents thf, pentane, toluene, and [D_6]benzene were stirred over sodium/benzophenone and distilled prior to use. **1**,[17,19] 2,7-di-*tert*-butyl-9-bromo-9-borafluorene,[18] and Li[P*t*Bu$_2$][20] were prepared according to the published procedures. The NMR spectra were recorded on a Bruker AM 250, a Bruker DPX 250, a Bruker Avance 300, and a Bruker Avance 400 spectrometer. NMR chemical shifts are reported in ppm. Elemental analyses were performed by the Microanalytical Laboratory of the Goethe University Frankfurt. Abbreviations: s = singlet; d = doublet; m = multiplet; br = broad; n.o. = not observed.

Synthesis of 2. A solution of Li[P*t*Bu$_2$][20] (157 mg, 1.03 mmol) in 3.5 mL of toluene was cooled to −30 °C, and 9-bromo-9-borafluorene (**1**)[17,19] (250 mg, 1.03 mmol), which was dissolved in 7.5 mL toluene, was added slowly. The reaction mixture was stirred at room temperature overnight and filtered. After removing all volatiles *in vacuo* the phosphaboradibenzofulvene **2** was obtained as a red oil. ^{1}H NMR (400.1 MHz, C_6D_6): δ 1.41 (d, $^3J_{HP}$ = 12.1 Hz, 18 H, *t*Bu), 6.92 (m, 2 H, Ar−H), 7.00 (m, 2 H, Ar−H), 7.08 (m, 2 H, Ar−H), 8.01 (m, 2 H, Ar−H). ^{11}B{^{1}H} NMR (128.4 MHz): δ 79.1 (br). ^{31}P{^{1}H} NMR (162.0 MHz, C_6D_6): δ 21.1 (br). ^{13}C{^{1}H} NMR (62.9 MHz, C_6D_6): δ 33.1 (d, $^1J_{PC}$ = 16.4 Hz, C(CH$_3$)$_3$), 33.8 (d, $^2J_{PC}$ = 11.8 Hz, C(CH$_3$)$_3$), 119.6 (d, $^4J_{PC}$ = 0.4 Hz, Ar−C), 128.3 (d, $^4J_{PC}$ = 1.0 Hz, Ar−C), 134.0 (d, $^5J_{PC}$ = 1.0 Hz, Ar−C), 137.4 (d, $^3J_{PC}$ = 3.4 Hz, Ar−C), 145.9 (br, B−C), 152.7 (d, $^3J_{PC}$ = 7.4 Hz, Ar−C). For assignment see Figures 6S and 12S in the Supporting Information. Anal. Calcd for $C_{20}H_{26}BP$ (308.21): C 77.94; H 8.50. Found: C 75.95; H 8.68. UV−vis (toluene): λ_{max} 478 nm. For spectrum see Figure 5S in the Supporting Information.

Synthesis of the tBu Derivative of **2**, *2,7-Di-tert-butyl-9-di-tertbutylphosphanyl-9-borafluorene.* A solution of 2,7-di-*tert*-butyl-9-bromo-9-borafluorene[18] (50 mg, 0.14 mmol) in 1 mL of C_6D_6 was slowly added to one molar equiv of Li[P*t*Bu$_2$][20] (22 mg, 0.14 mmol) dissolved in 0.5 mL of C_6D_6. The reaction mixture was stirred at room temperature for 75 min under the exclusion of air and then filtered. After removing all volatiles under vacuum 2,7-di-*tert*-butyl-9-di-*tert*-butylphosphanyl-9-borafluorene was obtained as a red oil. ^{1}H NMR

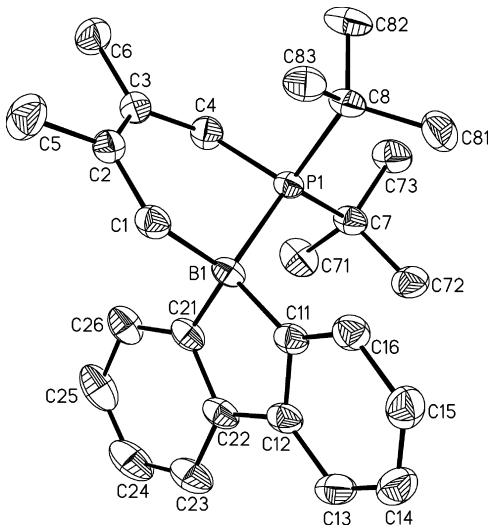


Figure 8. Solid-state structure of the Diels−Alder adduct **8**, which was obtained from the reaction of **2** with 2,3-dimethylbutadiene (monoclinic, $P2_1/c$). Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg): B(1)−P(1) = 1.9882(17), B(1)−C(1) = 1.635(2), B(1)−C(11) = 1.620(2), B(1)−C(21) = 1.625(2), P(1)−C(4) = 1.8141(16), P(1)−C(7) = 1.8831(16), P(1)−C(8) = 1.8903(16), C(1)−C(2) = 1.513(2), C(2)−C(3) = 1.340(2), C(3)−C(4) = 1.519(2); C(11)−B(1)−C(21) = 99.02(13), C(11)−B(1)−P(1) = 113.10(11), C(21)−B(1)−P(1) = 111.01(11), C(1)−B(1)−C(21) = 110.12(13), C(7)−P(1)−C(8) = 110.57(7), C(7)−P(1)−B(1) = 116.34(7), C(8)−P(1)−B(1) = 115.73(7), C(8)−P(1)−C(4) = 105.53(8), C(1)−C(2)−C(3) = 126.48(14), C(2)−C(3)−C(4) = 124.97(14); C(1)−C(2)−C(3)−C(4) = 4.7(3).

(300.0 MHz, C_6D_6): δ 1.27 (s, 18 H, Ar−*t*Bu), 1.49 (d, $^3J_{HP}$ = 11.9 Hz, 18 H, P−*t*Bu), 7.17−7.18 (m, 4 H, Ar−H), 8.19−8.20 (m, 2 H, Ar−H); see Figure 7S in the Supporting Information. ^{11}B{^{1}H} NMR (96.3 MHz): δ 78.4 (br). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ 21.0 (br). ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6): δ 31.4 (s, Ar−C(CH$_3$)$_3$), 33.0 (d, $^1J_{PC}$ = 16.3 Hz, P−C(CH$_3$)$_3$), 33.8 (d, $^2J_{PC}$ = 11.8 Hz, P−C(CH$_3$)$_3$), 34.9 (s, Ar−C(CH$_3$)$_3$), 119.1 (s, Ar−C), 130.9 (s, Ar−C), 135.2 (d, $^3J_{PC}$ = 3.2 Hz, Ar−C), 146.2 (br, B−C), 150.3 (d, $^3J_{PC}$ = 7.4 Hz, Ar−C), 150.5 (s, Ar−C). For assignment see Figures 7S and 13S in the Supporting Information.

Reaction of 2 with H_2. A solution of the phosphaboradibenzofulvene **2** (58 mg, 0.19 mmol) in 2 mL of toluene was stirred in an atmosphere of H_2 (1 atm) for 120 min at room temperature. The red color of **2** immediately disappeared. The NMR spectra of the reaction solution revealed that the hydrogen addition product **4** was formed in 50% yield.

Independent Synthesis of **4**. A solution of HP*t*Bu$_2$ (0.3 mL, 0.41 M, 0.12 mmol) in C_6D_6 was added to a freshly prepared solution of 9*H*-9-borafluorene[17] (0.12 mmol) in 0.3 mL of C_6D_6. The reaction mixture was stirred at room temperature for 60 min. NMR spectroscopic control showed a quantitative conversion to **4**. All volatiles were removed under vacuum. **4** was obtained by crystallization from a 1:1 mixture of toluene/pentane at −30 °C. Yield: 23 mg (0.07 mmol, 60%). X-ray quality crystals of **4** were obtained by slow evaporation of a benzene solution. ^{1}H NMR (300.0 MHz, C_6D_6): δ 0.84 (d, $^3J_{HP}$ = 13.6 Hz, 18 H, *t*Bu), 3.46 (br, 1 H, B−H), 4.03 (d, $^1J_{HP}$ = 357 Hz, 1 H, P−H), 7.31−7.41 (m, 4 H, Ar−H), 7.74−7.78 (m, 2 H, Ar−H), 7.90−7.93 (m, 2 H, Ar−H). ^{11}B{^{1}H} NMR (96.3 MHz): δ −20.5 (d, $^1J_{BP}$ = 45 Hz). ^{11}B NMR (96.3 MHz): δ −20.5 (dd, $^1J_{BP}$ = 45 Hz, $^1J_{BH}$ = 87 Hz). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ 42.3 (d, $^1J_{BP}$ = 45 Hz). ^{31}P NMR (121.5 MHz, C_6D_6): δ 42.3 (dm, $^1J_{HP}$ = 357 Hz). ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6): δ 29.2 (d, $^2J_{PC}$ = 1.0 Hz, C(CH$_3$)$_3$), 32.6 (d, $^1J_{PC}$ = 22.0 Hz, C(CH$_3$)$_3$), 120.4 (s,

dx.doi.org/10.1021/om400553j | *Organometallics* XXXX, XXX, XXX−XXX

Ar−C), 125.9 (d, $^4J_{PC}$ = 2.6 Hz, Ar−C), 126.3 (d, $^5J_{PC}$ = 2.3 Hz, Ar−C), 132.0 (d, $^3J_{PC}$ = 2.4 Hz, Ar−C), 150.6 (d, $^3J_{PC}$ = 8.6 Hz; Ar−C), 154.7 (br, B−C). For assignment see Figures 8S and 14S in the Supporting Information. Anal. Calcd for $C_{20}H_{28}BP$ (310.22): C 77.43; H 9.10. Found: C 76.19; H 9.03.

Remark: No release of H_2 was observable when **4** was heated to 120 °C.

Reaction of 2 with Acetonitrile. Acetonitrile (0.2 mL, 3.8 mmol) was added via syringe to a solution of the phosphaboradibenzofulvene **2** (0.18 mmol) in 2 mL of toluene at room temperature with stirring, whereupon the red solution turned colorless. The reaction mixture was concentrated to 1 mL and stored at 6 °C to obtain X-ray quality crystals of *cis*-**6** and *trans*-**6** (ratio 2:1) (monoclinic space group $P2_1/c$).

Performing this reaction with slowly added 2 equiv (20 μL, 0.38 mmol) of acetonitrile and **2** (0.18 mmol) in 6 mL of toluene yielded pure *trans*-**6** by storing the concentrated solution (1 mL) at −30 °C (triclinic space group $P\bar{1}$). In both reactions the yield was less than 10%. NMR spectra of *trans*-**6**: ^{1}H NMR (250.1 MHz, C_6D_6): δ 0.75 (d, $^3J_{HP}$ = 11.6 Hz, 36 H, *t*Bu), 1.69 (s, 6 H, CH_3), 7.27−7.40 (m, 8 H, Ar−H), 7.76−7.79 (m, 4 H, Ar−H), 8.14−8.16 (m, 4 H, Ar−H). ^{11}B{^{1}H} NMR (80.3 MHz, C_6D_6): δ 7.4 (br). ^{31}P{^{1}H} NMR (101.3 MHz, C_6D_6): δ 38.5 (br). ^{13}C{^{1}H} NMR (62.9 MHz, C_6D_6): δ 27.1 (d, $^2J_{PC}$ = 4.0 Hz, N=C(P*t*Bu$_2$)CH_3), 30.7 (d, $^2J_{PC}$ = 15.9 Hz, C(CH_3)$_3$), 32.7 (d, $^1J_{PC}$ = 29.7 Hz, *C*(CH_3)$_3$), 120.4 (s, Ar−C), 126.6 (s, Ar−C), 128.3 (s, Ar−C), 131.5 (s, Ar−C), 151.5 (d, $^5J_{PC}$ = 3.6 Hz; Ar−C), 188.5 (d, $^1J_{PC}$ = 48.2 Hz, N=*C*(P*t*Bu$_2$)CH_3), n.o. (*C*−B). For assignment see Figures 9S and 15S in the Supporting Information. Anal. Calcd for $C_{44}H_{58}B_2N_2P_2{\cdot}C_7H_8$ (790.65): C 77.47; H 8.41; N 3.54. Found: C 77.16; H 8.24; N 4.54.

Reaction of 2 with Benzophenone. A solution of the phosphaboradibenzofulvene **2** (0.18 mmol) in 2 mL of toluene was added to benzophenone (38 mg, 0.21 mmol). The red color of **2** disappeared within 30 s. The reaction mixture was stirred at room temperature overnight and filtered. All volatiles of the filtrate were removed under vacuum. X-ray quality crystals of **7** were grown from a 1:1 toluene/hexane solution at −30 °C. Yield: 18 mg (20%). ^{1}H NMR (300.0 MHz, C_6D_6): δ 1.20 (d, $^3J_{HP}$ = 10.4 Hz, 18 H, *t*Bu), 6.76 (m, 2 H, Ar−H), 6.93 (m, 6H, *m*,*p*-Ph), 7.02 (m, 2 H, Ar−H), 7.29 (m, 2 H, Ar−H), 7.67 (m, 2 H, Ar−H), 8.02 (m, 4 H, *o*-Ph). ^{11}B{^{1}H} NMR (96.3 MHz, C_6D_6): δ 46.9 ($h_{1/2}$ = 950 Hz). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ 91.1. ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6): δ 32.5 (d, $^2J_{PC}$ = 13.2 Hz, C(CH_3)$_3$), 36.4 (d, $^1J_{PC}$ = 36.2 Hz, *C*(CH_3)$_2$), 94.6 (d, $^1J_{PC}$ = 51.6 Hz; P*C*(O)Ph$_2$), 119.7 (s, Ar−C), 127.4 (d, $^4J_{PC}$ = 1.7 Hz, Ar−C), 127.6 (s, Ar−C), 128.0 (s, Ar−C), 129.1 (d, $^3J_{PC}$ = 10.2 Hz, Ar−C), 130.3 (s, Ar−C), 132.2 (s, Ar−C), 138.2 (s, Ar−C), 143.3 (d, $^2J_{PC}$ = 12.3 Hz, Ar−C), 153.1 (s, Ar−C). For assignment see Figures 10S and 16S in the Supporting Information. Anal. Calcd for $C_{33}H_{36}BOP$ (490.42): C 80.82; H 7.40. Found: C 79.02; H 7.44.

Reaction of 2 with DMB. A Schlenk tube was charged with the phosphaboradibenzofulvene **2** (0.28 mmol). **2** was dissolved in 3 mL of toluene, and DMB (145 mg, 1.77 mmol) was added. The red color of **2** disappeared after 2 h at room temperature. After stirring the reaction mixture overnight at room temperature all volatiles were removed under vacuum. The NMR spectra showed quantitative formation of **8**. X-ray quality crystals were obtained from a concentrated solution of toluene and pentane (1:1) at −30 °C. Yield: 49 mg (46%). ^{1}H NMR (400.1 MHz, C_6D_6): δ 0.84 (d, $^3J_{HP}$ = 12.0 Hz, 18 H, *t*Bu), 1.73 (s, CH_3), 1.77−1.83 (m, 5 H, B−CH_2 and CH_3), 2.44 (d, $^2J_{HP}$ = 11.1 Hz, 2 H, P−CH_2), 7.29 (m, 2 H, Ar−H), 7.36 (m, 2 H, Ar−H), 7.81 (m, 2 H Ar−H), 7.88 (m, 2 H, Ar−H). ^{11}B{^{1}H} NMR (96.3 MHz, C_6D_6): δ −13.6. ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ 11.7. ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6): δ 22.0 (d, $^1J_{PC}$ = 25.1 Hz, P−*C*H$_2$), 23.1 (d, $^3J_{PC}$ = 7.7 Hz, C=C(H)*C*H$_3$), 24.1 (d, $^4J_{PC}$ = 2.2 Hz, C=C(H)*C*H$_3$), 29.6 (d, $^2J_{PC}$ = 1.16 Hz, C(*C*H$_3$)$_3$), 33.4 (d, $^2J_{PC}$ = 12.0 Hz, B−*C*H$_2$), 35.0 (d, $^1J_{PC}$ = 19.6 Hz, *C*(CH$_3$)$_3$), 117.6 (d, $^3J_{PC}$ = 3.6 Hz; C=C), 120.0 (d, $^4J_{PC}$ = 1.1 Hz; Ar−C), 126.1 (d, $^4J_{PC}$ = 2.6 Hz, Ar−C), 126.6 (d, $^5J_{PC}$ = 2.4 Hz, Ar−C), 131.9 (d, $^3J_{PC}$ = 2.1 Hz, Ar−C), 136.7 (d, $^2J_{PC}$ = 8.7 Hz, C=C), 149.8 (d, $^3J_{PC}$ = 6.2 Hz, Ar−C), 159.1 (br, Ar−C). For assignment see Figures 11S and 17S in the Supporting Information. Anal. Calcd for $C_{26}H_{36}BP$ (390.35): C 80.00; H 9.30. Found: C 80.46; H 9.49.

X-ray Crystallography of 3, 4, *cis*-6/*trans*-6, *trans*-6, 7, and 8. The data for all structures were measured on a STOE IPDS-II diffractometer using a Genix Microfocus X-ray source with mirror optics and Mo Kα radiation. The data were corrected for absorption with the frame-scaling procedure contained in the X-AREA package. The structures were solved by direct methods using the program SHELXS and refined against F^2 with full-matrix least-squares techniques using the program SHELXL.[27] Hydrogen atoms were placed on ideal positions and refined with fixed isotropic displacement parameters using a riding model (for X-ray parameters see Table 1S and Table 2S in the Supporting Information). In **4** the H atoms bonded to B and P were freely refined. The toluene solvent in *trans*-**6** is disordered about a center of inversion over two equally occupied positions. The cif of **3** is available from the CSD, where it has been deposited as "Personal Communications", J. M. Breunig, A. Hübner, M. Bolte, M. Wagner, and H.-W. Lerner, 2013, CCDC 938237. CCDC reference numbers: CCDC 938239 (**4**), CCDC 938238 (2:1 cocrystal of *cis*-**6** and *trans*-**6**), CCDC 943018 (*trans*-**6**), CCDC 941398 (**7**), and CCDC 942579 (**8**).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystal packing of *trans*-**6**, solid-state structure of *trans*-**6** in the 2:1 cocrystal of *cis*-**6** and *trans*-**6** (monoclinic, $P2_1/c$), ball-and-stick presentation of **3**, crystal packing of the phosphonium salt **3**, UV−vis spectrum of **2**, ^{1}H NMR spectra of **2** and of *t*Bu derivative of **2**, **4**, *trans*-**6**, **7**, and **8**, assignment of the signals of the NMR spectra of **2**, *t*Bu derivative of **2**, **4**, *trans*-**6**, **7**, and **8**, and the table of X-ray parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Fax: +49-69798-29260. E-mail: lerner@chemie.uni-frankfurt.de.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

A.H. wishes to thank the Fonds der Chemischen Industrie for a Ph.D. grant. This work was supported by the Beilstein-Institut, Frankfurt/Main (Germany), within the research collaboration NanoBiC.

■ REFERENCES

(1) Paine, R. T.; Nöth, H. *Chem. Rev.* **1995**, *95*, 343−379. Power, P. P. *Chem. Rev.* **1999**, *99*, 3463−3503.

(2) Pestana, D. C.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 8426−8437.

(3) Dias, H. V. R.; Power, P. P. *J. Am. Chem. Soc.* **1989**, *111*, 144−148. Dias, H. V. R.; Power, P. P. *Angew. Chem., Int. Engl.* **1987**, *26*, 1270−1271. Pestana, D. C.; Power, P. P. *Organometallics* **1992**, *11*, 98−103. Bartlett, R. A.; Dias, H. V. R.; Feng, X.; Power, P. P. *J. Am. Chem. Soc.* **1989**, *111*, 1306−1311. Bartlett, R. A.; Feng, X.; Power, P. P. *J. Am. Chem. Soc.* **1986**, *108*, 6817−6819.

(4) Bartlett, R. A.; Dias, H. V. R.; Power, P. P. *Inorg. Chem.* **1988**, *27*, 3919−3922. Nöth, H.; Staude, S.; Thomann, M.; Paine, R. T. *Chem. Ber.* **1993**, *126*, 611−618.

(5) Karsch, K.; Hanika, G.; Huber, B.; Meindl, K.; König, S.; Krüger, C.; Müller, G. *Chem. Commun.* **1989**, 373−375.

(6) Linti, G.; Nöth, H.; Polborn, K.; Paine, R. T. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 682−684.

(7) Rivard, E.; Merrill, W. A.; Fettinger, J. C.; Power, P. P. *Chem. Commun.* **2006**, 3800−3802.
(8) Tsurusaki, A.; Sasamori, T.; Wakamiya, A.; Yamaguchi, S.; Nagura, K.; Irle, S.; Tokitoh, N. *Angew. Chem., Int. Ed.* **2011**, *50*, 10940−10943.
(9) Four-membered P2B2 rings see, for example: Scheschkewitz, D.; Amii, H.; Gornitzka, H.; Schoeller, W. W.; Bourissou, D.; Bertrand, G. *Science* **2002**, *295*, 1880−1881. Scheschkewitz, D.; Amii, H.; Gornitzka, H.; Schoeller, W. W.; Bourissou, D.; Bertrand, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 585−587. Rodriguez, A.; Tham, F. S.; Schoeller, W. W.; Bertrand, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 4876−4680. Bourg, J.-B.; Rodriguez, A.; Scheschkewitz, D.; Gornitzka, H.; Bourissou, D.; Bertrand, G. *Angew. Chem., Int. Ed.* **2007**, *46*, 5741−5745. Gandon, V.; Bourg, J.-B.; Tham, F. S.; Schoeller, W. W.; Bertrand, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 155−159. Amii, H.; L. Vranicar, L.; Gornitzka, H.; Bourissou, D.; Bertrand, G. *J. Am. Chem. Soc.* **2004**, *126*, 1344−1345. Fuks, G.; Saffon, N.; Maron, L.; Bertrand, G.; Bourissou, D. *J. Am. Chem. Soc.* **2009**, *131*, 13681−13689. Dou, D.; Linti, G.; Chen, T.; Duesler, E. N.; Paine, R. T.; Nöth, H. *Inorg. Chem.* **1996**, *35*, 3626−3634. Chen, T.; Duesler, E. N.; Paine, R. T.; Nöth, H. *Inorg Chem.* **1997**, *36*, 1070−1075. Knabel, K.; Klapötke, T. M.; Nöth, H.; Paine, R. T.; Schwab, I. *Eur. J. Inorg. Chem.* **2005**, 1099−1108. Kaufmann, B.; Nöth, H.; Paine, R. T.; Polborn, K.; Thomann, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *43*, 1446−1448.
(10) Geier, S. J.; Gilbert, T. M.; Stephan, D. W. *J. Am. Chem. Soc.* **2008**, *130*, 12632−12633.
(11) Geier, S. J.; Gilbert, T. M.; Stephan, D. W. *Inorg. Chem.* **2011**, *50*, 336−344.
(12) Dornhaus, F.; Scholz, S.; Sänger, I.; Bolte, M.; Wagner, M.; Lerner, H.-W. *Z. Anorg. Allg. Chem.* **2009**, *635*, 2263−2272.
(13) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y.-M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667−5672.
(14) Wiberg, N.; Wagner, G.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 229−230.
(15) Lerner, H.-W. *ChemInform* **2005**, *36*, DOI 10.1002/chin.200540290. Lerner, H.-W. *Recent Res. Dev. Org. Chem.* **2004**, *8*, 159−196.
(16) Wiberg, N.; Wagner, S.; Vasisht, S.-K. *Chem.—Eur. J.* **1998**, *4*, 2571−2579. Wiberg, N.; Hwang-Park, H.-S.; Lerner, H.-W.; Dick, S. *Chem. Ber.* **1996**, *129*, 471−478. Meyer-Wegner, F.; Wender, J. H.; Falahati, K.; Porsch, T.; Sinke, T.; Bolte, M.; Wagner, M.; Holthausen, M. C.; Lerner, H.-W. Unpublished results.
(17) Hübner, A.; Qu, Z.-W.; Englert, U.; Bolte, M.; Lerner, H.-W.; Holthausen, M. C.; Wagner, M. *J. Am. Chem. Soc.* **2011**, *133*, 4596−4609.
(18) Hübner, A.; Diefenbach, M.; Bolte, M.; Lerner, H.-W.; Holthausen, M. C.; Wagner, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 12514−12518.
(19) Hübner, A.; Lerner, H.-W.; Wagner, M.; Bolte, M. *Acta Crystallogr.* **2010**, *E66*, o444. Mewes, J.; Lerner, H.-W.; Bolte, M. *Acta Crystallogr.* **2009**, *E65*, o451.
(20) Scholz, S.; Bolte, M.; Wagner, M.; Lerner, H.-W. *Z. Anorg. Allg. Chem.* **2007**, *633*, 1199−1204.
(21) Fulvenes are yellow-red and oily compounds: Beyer, H.; Walter, W.; Lloyd, D. *Organic Chemistry: A Comprehensive Degree Text and Source Book*; Woodhead Publishing, 1997. Hafner, K.; Häfner, K. H.; König, C.; Kreuder, M.; Ploss, G.; Schulz, G.; Sturm, E.; Vöpel, K. H. *Angew. Chem.* **1963**, *75*, 35−46.
(22) Gilbert, T. M.; Bachrach, S. M. *Organometallics* **2007**, *26*, 2672−2678.
(23) For 1,4-addition reactions of frustrated Lewis pairs to 1,3-dienes see: Ullrich, M.; Seto, K. S.-H.; Lough, A. J.; Stephan, D. W. *Chem. Commun.* **2009**, 2335−2337.
(24) Cambridge Structural Database (CSD, Version 5.32 with three updates, November 2010; Allen, 2002). Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380.
(25) Jennings, J. R.; Snaith, R.; Mahmoud, M. M.; Wallwork, S. C.; Bryan, S. J.; Halfpenny, J.; Petch, E. P.; Wade, K. *J. Organomet. Chem.* **1983**, *249*, Cl−C5. Halfpenny, J. *Acta Crystallogr.* **1989**, *C45*, 1453−1454. Lesley, M. J. G.; Pineau, M. R.; Nelson, D. M.; Crundwell, G. *Acta Crystallogr.* **2007**, *E63*, o1204−o1206.
(26) Hayek, A.; Nicoud, J.-F.; Bolze, F.; Bourgogne, C.; Baldeck, P. L. *Angew. Chem., Int. Ed.* **2006**, *45*, 6466−6469. Britton, D.; Emerson, K. *J. Chem. Cryst.* **1999**, *29*, 841−843.
(27) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112−122.